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RPPR Final Report
as of 06-Nov-2018

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Major Goals: 1) Use nanoscale analytical characterization to understand and quantify the post-synthetic modification (PSM) of MOFs to develop viable synthesis routes for obtaining complex, novel MOF nanostructures with tailored functionality.?PSM of conventional MOF nanostructures has been widely reported for a variety of MOF systems and exchange species, both metal nodes and ligands, based on bulk-averaged and indirect characterization methods, such a PXRD, SEM-EDs, N2 sorption analysis, NMR, and ICP-MS/OES. However, MOF formation and the subsequent reactivity of the structural elements of MOFs has not been examined with nanoscale resolution and in individual crystal. High-resolution TEM imaging combined with STEM energy dispersive X-ray spectroscopy (EDS) elemental mapping provides a unique method for detailed structural and chemical analysis of these processes through direct characterization of single MOF crystals. Expected outcomes include a detailed understanding of the true extent of PME in individual MOF nanocrystals, and the pathways involved in such exchange processes. It is also possible we uncover alternative modification pathways, other than true “exchange,” which have not been previously considered.
2) Combine nanoscale experimental observation (in situ ETEM) with theoretical models of the absorption and sequestration of small molecules (“breathing”) in MOFs during environmental changes.?Absorption of gases by MOFs is of great interest for the sequestration and remediation of gaseous toxins. However, these absorb/release processes in real MOFs, which are nanoscale crystals, is largely unknown. Previously under this grant, we have developed lattice models of MOF “breathing,” and here we seek to correlate our models with direct in situ characterization during breathing, using ETEM gas cycling and heat ramping while monitoring the transformation of individual MOF nanocrystals. Through this experimental and theoretical approach, we aim to understand molecular absorption-and-release phenomena in prototypical MOFs, and establish this methodology as a widely-adopted approach for studying similar processes in porous nanomaterials generally. A detailed analysis of crystal morphology and defects and how they develop, change, or affect these processes, will be a key part of this work and will be studied both experimentally and theoretically.

Accomplishments: See uploaded document.

Training Opportunities: See uploaded report.

Results Dissemination: See uploaded report.

RPPR Final Report
as of 06-Nov-2018

Honors and Awards: Since July 2015, the PI, Prof. Seth Cohen, has been awarded several honors and awards, namely: the 2018 Freeman Lectureship (U. Sydney, Australia), the 2018 Research Corporation TREE Award, the 2017 Chancellor's Award for Excellence in Postdoctoral Scholar Mentoring, the 2016 Arthur C. Cope Scholar Award from the American Chemical Society (ACS), among others. The PI also held the position of the Leslie E. Orgel Faculty Scholar in Inorganic Chemistry at U.C. San Diego from 2015-2018. One of the trainees on the award, Dr. Michael Denny (who graduated in 2018), also garnered several accolades including a 2015 ARCS Foundation Scholarship, a 2016 Distinguished Graduate Student Fellowship from U.C. San Diego, and a 2017 Graduate Student Association Travel Award.

The co-PI, Prof. Francesco Paesani, was the recipient of the 2016 Early Career Award in Theoretical Chemistry from the ACS Division of Physical Chemistry.

The co-PI, Prof. Nathan Gianesschi, was named a 2016 Fellow of the Royal Society of Chemistry and was a finalist for the 2017 Blavatnik Young Scientist Award. His trainee, Mollie Touve, was awarded a NDSEG fellowship and received an honorable mention for the NSF graduate research fellowship in 2016.

These accomplishments are representative (and not comprehensive) of some of the recognition that this highly productive research team has achieved.

Protocol Activity Status:

Technology Transfer: Nothing to Report

Grants Agreement Award#: W911NF-15-1-0189

Final Progress Report for the period of July 1, 2015 and ending June 30, 2018

The Chemistry of Metal-Organic Frameworks Captured by STEM Elemental Analysis and Gas Phase in situ ETEM

RDRL-ROS-I Proposal Number: 66721-CH

Submitted to,
Army Research Office

By,
The University of California, San Diego

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July 31, 2018

Abstract
Metal-organic frameworks (MOFs) are self-assembled networks of inorganic nodes (metal ions or metal ion clusters often referred to as secondary building units, SBUs) bridged by multitopic organic ligands (i.e. linkers). MOFs are highly porous materials and are highly tunable by pre- or post-synthetic methods. MOFs have attracted great attention as materials for gas storage, separation, catalysis, and other uses. To date, there have been few studies on MOF formation, partly due to difficulties in analyzing the formation of the particles as they assemble and precipitate from solution, leaving a large gap in the understanding of mechanisms underlying the formation of these important materials such as how to precisely control and tune the porosity or final morphology. It is of course, precisely these properties of the materials that make them important and interesting. Furthermore, as MOF defects and nanoscale morphologies have been shown to be important for bulk properties, having a method to both analyze MOF formation and defects would be highly desirable in optimizing their synthesis or post-synthetic modification. Here we propose that (scanning) transmission electron microscopy (S)TEM, both analytical and in situ (environmental gas-phase and/or heating) can be used to observe the precise nanoscale structure of MOFs after synthesis or modification (lattice-structure, morphology and elemental composition), and during complex functional processes such as the absorption and release of small molecules. Such studies will give unparalleled information about the fundamental mechanisms of formation, and the behavior of individual particles, information that can be used toward the development of specifically optimized functional MOFs.

Objectives

1) Use nanoscale analytical characterization to understand and quantify the post-synthetic modification (PSM) of MOFs to develop viable synthesis routes for obtaining complex, novel MOF nanostructures with tailored functionality. PSM of conventional MOF nanostructures has been widely reported for a variety of MOF systems and exchange species, both metal nodes and ligands, based on bulk-averaged and indirect characterization methods, such a PXRD, SEM-EDs, N_2 sorption analysis, NMR, and ICP-MS/OES. However, MOF formation and the subsequent reactivity of the structural elements of MOFs has not been examined with nanoscale resolution and in individual crystal. High-resolution TEM imaging combined with STEM energy dispersive X-ray spectroscopy (EDS) elemental mapping provides a unique method for detailed structural and chemical analysis of these processes through direct characterization of single MOF crystals. Expected outcomes include a detailed understanding of the true extent of PME in individual MOF nanocrystals, and the pathways involved in such exchange processes. It is also possible we uncover alternative modification pathways, other than true “exchange,” which have not been previously considered.

2) Combine nanoscale experimental observation (*in situ* ETEM) with theoretical models of the absorption and sequestration of small molecules (“breathing”) in MOFs during environmental changes. Absorption of gases by MOFs is of great interest for the sequestration and remediation of gaseous toxins. However, these absorb/release processes in real MOFs, which are nanoscale crystals, is largely

unknown. Previously under this grant, we have developed lattice models of MOF "breathing," and here we seek to correlate our models with direct *in situ* characterization during breathing, using ETEM gas cycling and heat ramping while monitoring the transformation of individual MOF nanocrystals. Through this experimental and theoretical approach, we aim to understand molecular absorption-and-release phenomena in prototypical MOFs, and establish this methodology as a widely-adopted approach for studying similar processes in porous nanomaterials generally. A detailed analysis of crystal morphology and defects and how they develop, change, or affect these processes, will be a key part of this work and will be studied both experimentally and theoretically.

3) Use lattice-resolution TEM characterization and in situ liquid-cell (LC)TEM observations to understand and quantify the nanoscale formation of polymer-MOF hybrid structures (polyMOFs). This new objective builds on the findings developed in this research program to apply toward a new class of porous materials referred to as polyMOFs. These studies will help us to develop viable synthesis routes for obtaining complex, novel MOF nanostructures with tailored functionality. Preliminary findings on this new objective are described in this report.

Training

Throughout this program, students and researchers have had numerous training opportunities. Participants have received training in a wide range of techniques, including chemical synthesis, spectroscopic methods, X-ray diffraction, TEM imaging, and the like. Researchers have also received thorough training in laboratory safety and research ethics. Formal class instruction, such as courses on powder X-ray diffraction, have been included as part of the training for some researchers. Participants have attended workshops and meetings, including those organized by the ARO, the MOF2016 conference, and regional and national American Chemical Society meetings. Professional development and networking opportunities have been made available to trainees on this award.

Results During This Reporting Period

Structural Analysis of polyMOFs to Understand Fundamental Growth Processes in this Class of Hybrid MOFs

Cohen and Gianneschi Laboratories

The Cohen lab had recently developed a novel class of hybrid MOF, termed **Poly-MOFs**, where the ligand units are not single discrete ligands connecting metal clusters as in conventional MOFs, but are instead long polymer chains of multiple adjoined ligands that weave together the metal clusters into crystalline framework lattices (**Figure 1**). (*Angew. Chem. Ind. Ed.*, **2015**, *54*, 6152). In previous studies, the Cohen lab has used PXRD to determine the framework structures of their polyMOFs, confirming that their structures match those of the conventional MOF analog, e.g. polyUiO-66 and UiO-66. (*Chem. Comm.* **2017**, *53*, 3058). However, the nanostructural details of the hierarchical poly-MOF particles are unknown, and how these hybrid MOFs form during synthesis remain a mystery.

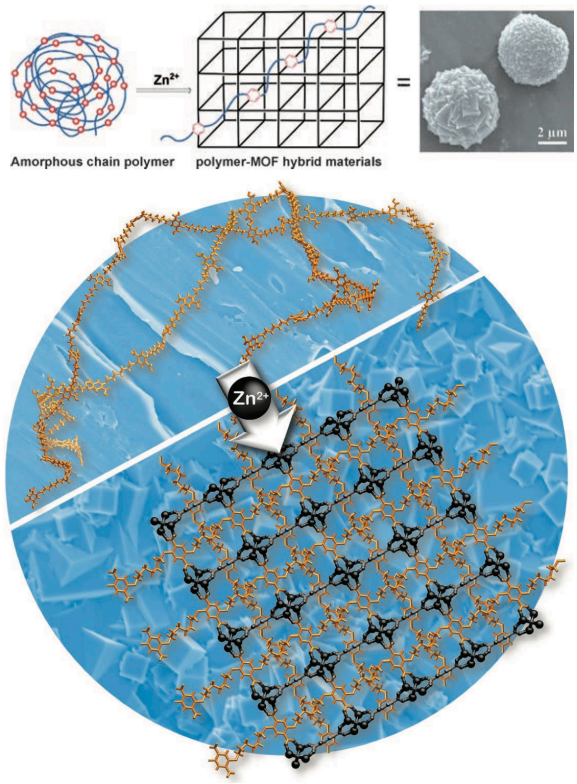

Figure 1. Poly-MOF lattices with the same lattice structure of their conventional MOF analog can be formed from polymerized versions of the ligand and the same metal clusters (*Angew. Chem. Ind. Ed.*, **2015**, *54*, 6152).

Experimental Protocol

General Information. All polymers and polyMOF materials were prepared as previously described (*Angew. Chem. Ind. Ed.*, **2015**, *54*, 6152; *Chem. Comm.* **2017**, *53*, 3058).

TEM Characterization. The formed Poly-UiO-66 particles were prepared on lacey-C TEM grids by drop casting 4 µL of a methanol solution containing the poly-UiO-66 particles. Prior to drop casting, the sample solution was sonicated for ~30 min to disperse the particles. TEM diffraction was done using a Hitachi 7700 TEM (200 kV), and High-resolution (HR)TEM imaging was done using a JEOL ARM300 (300 kV) operating at a dose rate of ~1 $e^-/Å^2s$ and using low dose imaging protocols to mitigate beam damage.

Results and Discussion. The intention of this study into polyMOFs, which is ongoing, is to use HRTEM imaging combined with in situ LCTEM videography to study the nucleation,

growth, and evolution processes that occur on the nanoscale and ultimate yield the complex, hierarchical polyMOF micron-scale particles (**Figure 1**, *Angew. Chem. Ind. Ed*., **2015**, *54*, 6152; *Chem. Comm.* **2017**, *53*, 3058). We seek to understand the formation pathways of these hybrid mesoporous materials and leverage this knowledge to create novel hybrid MOFs architectures and morphologies for tailored functional application. To address these questions, a series of polyMOF samples were prepared for HRTEM characterization and to determine target systems for in situ LCTEM studies. UiO-66(Zr) nanoparticles were synthesized by standard protocols using an acetic acid modulator to yield monodisperse particles of ca. 100 nm. polyUiO-66 hierarchical particles were synthesized following literature protocols (*Chem. Comm.* **2017**, *53*, 3058).

We first characterized the conventional (e.g., molecular ligand based) UiO-66 nanoparticles by HRTEM imaging and TEM diffraction to determine the standard lattice structure of the UiO-66 framework (**Figure 2**). These data serve as the control to which the polyUiO-66 structure data can be compared, to verify that our polyUiO-66 samples do have the characteristic framework structure of genuine UiO-66. Consistent with previous reports of conventional UiO-66, we measure predominant crystalline lattice spacings at *ca*. 1.14, 0.99, 0.71, 0.57, and 0.39 nm (*J. Am. Chem. Soc.* **2008**, *130*, 13850).

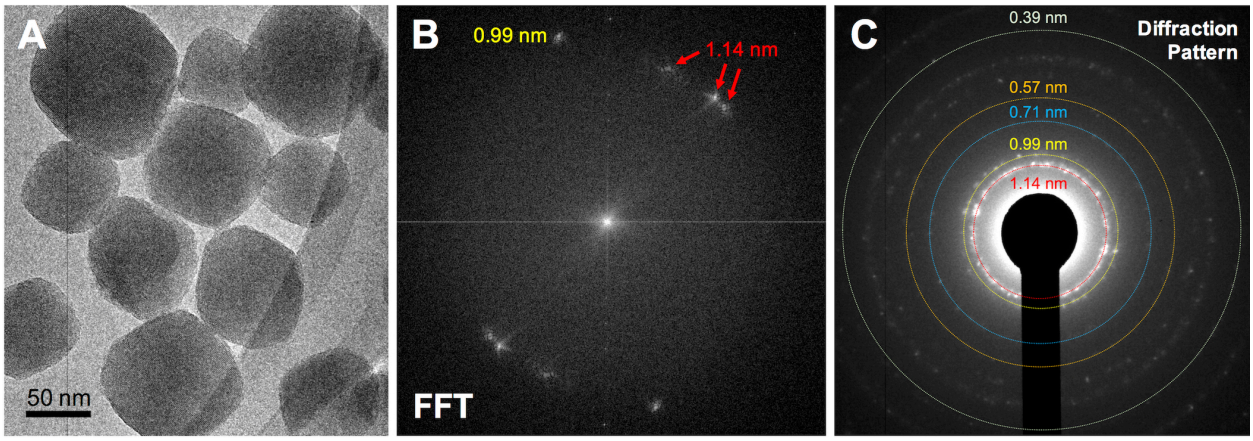

Figure 2. TEM characterization of conventional UiO-66 nanoparticles. **(A)** HRTEM image of UiO-66 single-crystalline particles. **(B)** Fast Fourier transform (FFT) of the image in **A**. FFT Spots generated from the lattice fringes of on-axis particles are identified. **(C)** TEM diffraction pattern of an ensemble of UiO-66 nanoparticles. Characteristic lattice spacings are identified by respective colored rings.

With an understanding of the UiO-66 structure, we have begun our *ex situ* TEM characterization studies of the polyUiO-66 hierarchical particles (**Figure 3** and **Figure 4**). Low magnification SEM imaging (Figure 3A-B) of the polyUiO-66 sample confirms that we have reproduced the hierarchical particles that have been previously reported (*Chem. Comm.* **2017**, *53*, 3058). Low magnification TEM imaging of these materials prepared on TEM grids indicates that the large particles are transferred to the support substrate (Figure 3C), though the hierarchical particles themselves are far too thick for HRTEM imaging or TEM diffraction. At the surface of, and adjacent to the large hierarchical polyUiO-66 particles are dispersed network of polyUiO-66 sub-particles freed from the larger particles during drop-casting and grid preparation (Figure 3D). These sub-particles

are the ideal size (<100 nm thick) for lattice resolution HRTEM imaging and diffraction structural characterization (**Figure 4**). TEM diffraction of regions of the network of sub-particles indicates the presence of multiple crystalline domains with the characteristic UiO-66 lattice structure (Figure 4A-B). Using HRTEM imaing (Figure 4C-D), we find that the UiO-66 crystalline domains are small, on the order of several tens of nanometers (*ca.* 20-50 nm). From our initial HRTEM data, it appears that in the sub-particles, the small crystalline domains are interconnected by amorphous polymer regions (non-poly-MOF), forming a hybrid crysalline-amphous structure. We are now starting TEM elemental mapping (spectroscopy) studies to determine if the regions we believe are amorphous are difficient in metal (Zr for poly-UiO-66) in compartison to the crystalline domains.

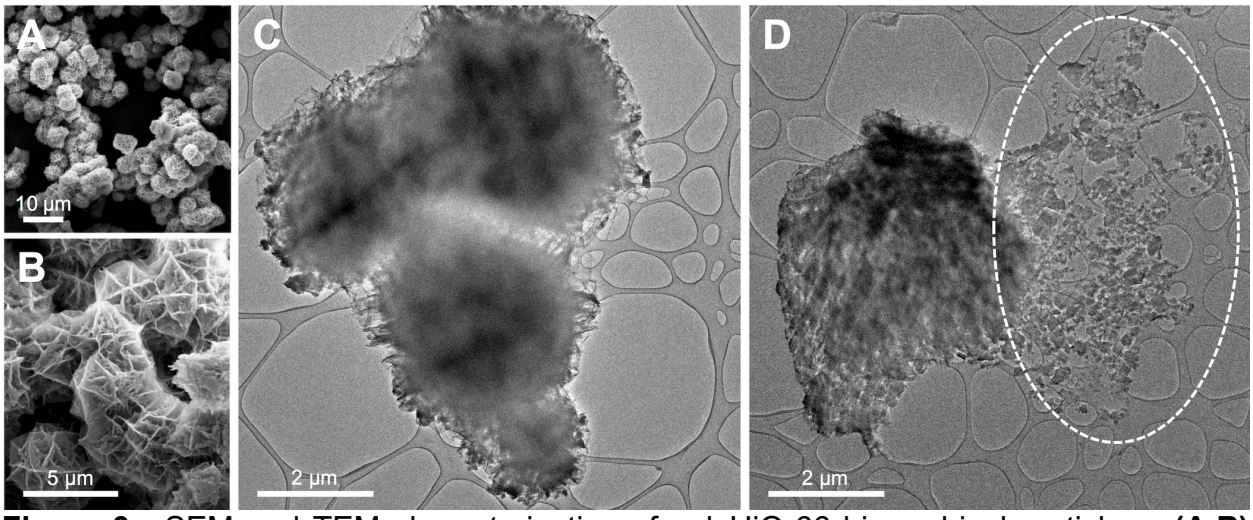

Figure 3. SEM and TEM characterization of polyUiO-66 hierarchical particles. **(A,B)** SEM images of the as synthesized polyUiO-66 particles. **(C,D)** Low-magnification TEM images of the as synthesized polyUiO-66 particles that have been drop cast on TEM grids. The large particles are far too thick for high-magnification TEM characterization. The white oval in D indicates a region adjacent to one large hierarchical particle where some sub-particles have been freed following sonication. HRTEM imaging (**Figure 4**) was done in this region of sub-particles where the material is sufficiently thin.

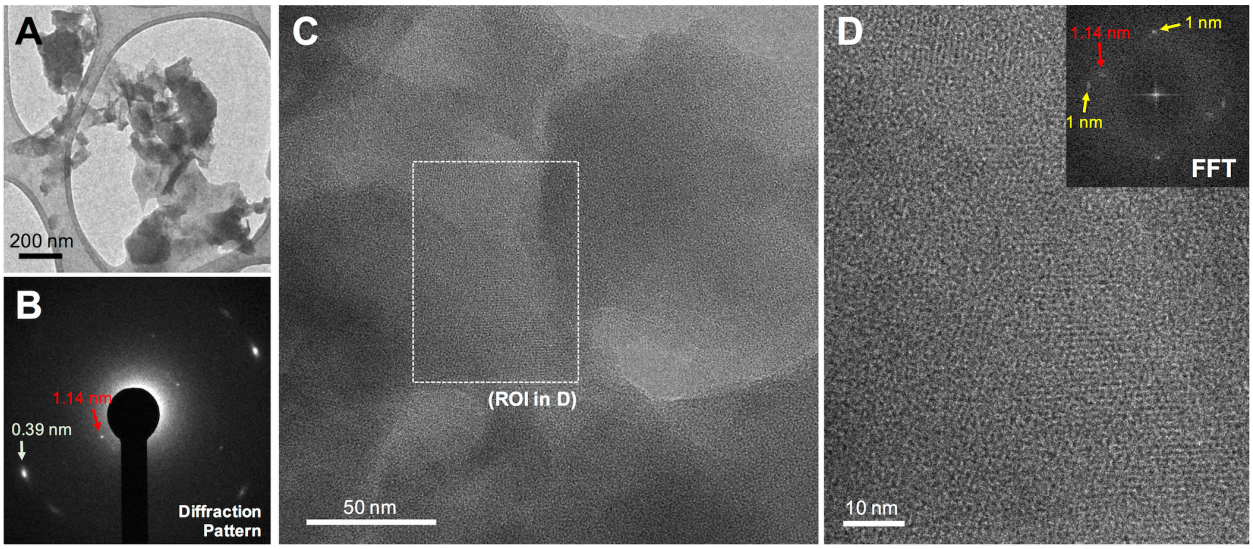

Figure 4. TEM characterization of Poly-UiO-66 framework lattice structure. **(A)** Low-magnification TEM image of poly-UiO-66 particles with some crystalline domains. **(B)** diffraction pattern of the region in **A**. Diffraction spots indicate the presence of crystalline domains withint these poly-UiO-66 sub-particles. The lattice spacings of the crystalline domains match those of conventional UiO-66 (**Figure 2**). (**C/D)** HRTEM lattice images of crystalline domains in the sub-particles. **(D)** enlarged region of interest (ROI) that is indicated by the white box in **C**. Lattice spacing are resolved (FFT inset confirms that the lattice spacing match those of conventional UiO-66). The size of the crystalline domains is ~20-50 nm. The sub-particles of poly-UiO-66 are composed of a polycrystalline-amorphous hybrid structure.

Deposition of Metal Oxide Coatings onto Metal-Organic Frameworks

Cohen and Gianneschi Laboratories

This work was described in detail in the prior interim report.

The work has now been published in:

Michael S. Denny, Jr., Lucas R. Parent, Joseph P. Patterson, Santosh Kumar Meena, Huy Pham, Patricia Abellan, Quentin M. Ramasse, Francesco Paesani, Nathan C. Gianneschi,* and Seth M. Cohen*, "Transmission Electron Microscopy Reveals Deposition of Metal Oxide Coatings onto Metal−Organic Frameworks" *J. Am. Chem. Soc*. **2018**, *140*, 1348-1357.

Small Molecule Absorption-Release ("Breathing") Studied by in situ Environmental (E)TEM and Lattice Modeling

Gianneschi, Cohen, and Paesani Laboratories

MOFs have emerged as an effective platform for the rational design of multifunctional materials, combining large specific surface areas with flexible, periodic frameworks that can undergo reversible structural transitions, or "breathing", upon temperature and pressure changes, and through gas adsorption/desorption processes. Although MOF breathing can be inferred from the analysis of adsorption isotherms, direct observation of the structural transitions has so far been lacking, and the underlying processes of framework-reorganization in individual MOF nanocrystals has remained largely unknown. As part of this research program, we combined *in situ* environmental transmission electron microscopy (ETEM) and computer simulations to elucidate MOF breathing at the microscopic level. The combined approach allowed us to directly monitor, for the first time, the breathing behavior of individual MIL-53(Cr) nanocrystals upon reversible water adsorption and temperature changes.

Our study, which appeared as a Communication in the Journal of the American Chemical Society (*J. Am. Chem. Soc.* **2017**, *139*, 13972) demonstrates that breathing induced by water adsorption in MIL-53(Cr) proceeds by (**Figure 5** and **Figure 6**; **Table 1** and **Table 2**): (1) the removal of extra organic linkers from the pore channels when in ultrahigh-vacuum and electron beam irradiation, with no change after the introduction of H_2O vapor, (2) upon heating to 300 ˚C (calcination), one H_2O molecule per unit cell is adsorbed in the pore channels (first lattice change), and (3) when the temperature is lowered back to 27 ˚C, an additional 24 H_2O molecules per unit cell are adsorbed in the pores (second lattice change). This breathing transition between 1 and 25 H_2O molecules is reversible by a heating-cooling cycle. Adsorption of one H_2O molecule per unit cell during the first calcination (heating to 300 ˚C) represents the initial step that activates the breathing effect, providing a means for including up to 25 H_2O molecules when subsequently cooled to 27 ˚C. As shown by the MD simulations, this activation step involves hydrogen bonding between the first adsorbed water molecules and the bridging μ-OH groups of the framework SBUs. By anchoring to the framework, these individual H_2O molecules become effective hydrogen bonding sites that facilitate the adsorption of additional water molecules when the material is cooled, and they remain when other water molecules are removed from the pores during subsequent heating.

By enabling the characterization of structural changes at the lattice level, our study effectively opens the door to future synergistic applications of *in situ* ETEM measurements and computer simulations to investigate the relationship between pore size/shape and host-guest interactions.

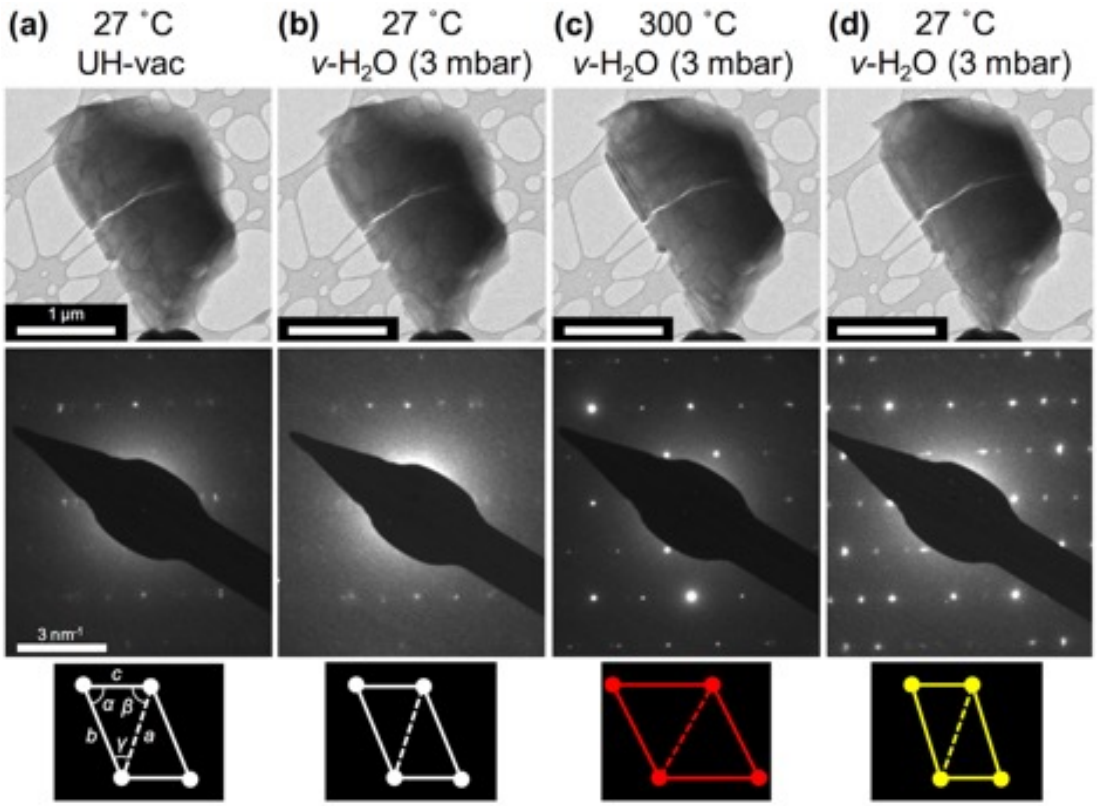

Figure 5. *In situ* ETEM images (top row) and diffraction patterns (middle row) of one MIL-53(Cr) nanocrystal at four different environmental conditions during breathing; (a) 27 ˚C and UH-vacuum, (b) 27 ˚C and water vapor ("pre-calcination"), (c) 300 ˚C and water vapor ("calcinated"), and (d) 27 ˚C and water vapor ("post-calcination"). The bottom row highlights the lengths (*a, b, c*) and angles (α, β, γ) between diffraction spots in the ETEM diffraction patterns (**Table 1**).

Table 1. Measured lengths and angles between the diffraction spots in the four experimental MIL-53(Cr) ETEM diffraction patterns during the "breathing" experiment in **Figure 5**.

ETEM conditions	*a* (nm^{-1})	*b* (nm^{-1})	*c* (nm^{-1})	*α* (deg)	*β* (deg)	*γ* (deg)
27 ˚C vacuum	1.66	1.72	1.16	67.3	72.4	40.4
27 ˚C H_2O vapor	1.66	1.72	1.16	67.3	72.4	40.4
300 ˚C H_2O vapor	1.82	1.77	1.7	63.2	60.3	56.5
27 ˚C H_2O vapor	1.71	1.68	1.04	73.7	70.6	35.7

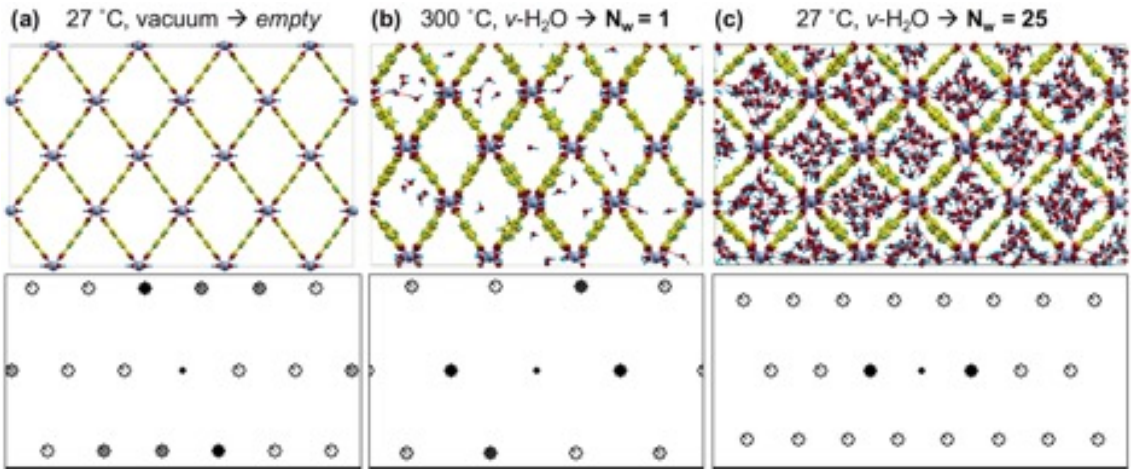

Figure 6. *In silico* transmission images (top row) of the MIL-53(Cr) lattice (here, visualized on the [322] zone axis) at the three different environmental conditions used in the ETEM breathing experiment (the guest molecules in (b) and (c) are H_2O). The bottom row are the simulated electron diffraction patterns from the three MIL-53(Cr) lattice models on the [322] zone axis. These three simulated diffraction patterns were measured (**Table 2**) and used in the analysis of the ETEM diffraction data.

Table 2. Lengths and angles between the diffraction spots in the three simulated diffraction patterns obtained from MD simulations of MIL-53(Cr) on the [322] zone axis at different environmental conditions (mimicking ETEM conditions in **Figure 5** and **Table 1**), corresponding with a variable number of water molecules adsorbed per unit cell.

MD conditions	*a* (nm^{-1})	*b* (nm^{-1})	*c* (nm^{-1})	*α* (deg)	*β* (deg)	*γ* (deg)	H_2O
27 ˚C vacuum	1.66	1.77	1.13	65.74	75.97	38.3	**0**
27 ˚C H_2O vapor	-	-	-	-	-	-	**-**
300 ˚C H_2O vapor	1.87	1.82	1.68	64.27	61.51	54.22	**1**
27 ˚C H_2O vapor	1.64	1.61	1.11	71.85	68.48	39.67	**25**

The work has now been published in:

Lucas R. Parent, Huy Pham, Joseph P. Patterson, Michael S. Denny, Jr., Seth M. Cohen, Nathan C. Gianneschi*, and Francesco Paesani*, "Pore Breathing of Metal-Organic Frameworks by Environmental Transmission Electron Microscopy" *J. Am. Chem. Soc.* **2017**, *139*, 13973-13976.

Summary and Future Work

This concludes the project. With four published manuscripts in top journals and the majority of the objectives met, we hope the sponsors are satisfied with our results. In continuing projects, we hope to expand on our polyMOF findings, as well as use in situ TEM to explore exchange phenomena in MOF materials